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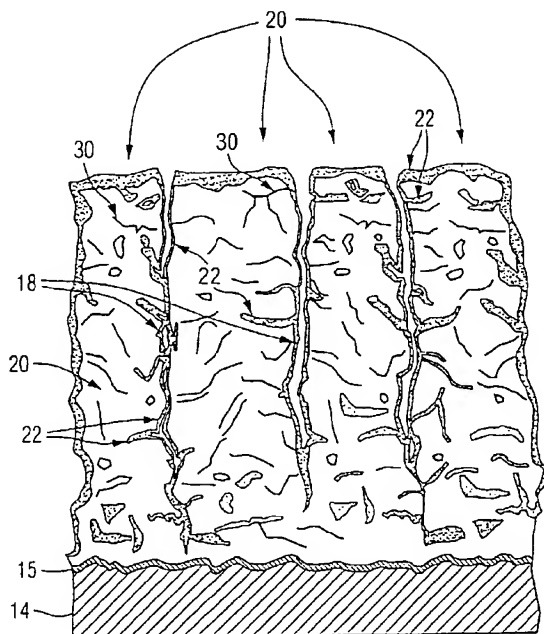
(43) International Publication Date
4 April 2002 (04.04.2002)

PCT

(10) International Publication Number
WO 02/27066 A2

- (51) International Patent Classification⁷: **C23C 28/00**
- (21) International Application Number: **PCT/US01/24238**
- (22) International Filing Date: **2 August 2001 (02.08.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
09/640,073 **17 August 2000 (17.08.2000)** **US**
- (71) Applicant: **SIEMENS WESTINGHOUSE POWER CORPORATION [US/US]; 4400 Alafaya Trail, Orlando, FL 32826-2399 (US).**
- (72) Inventors: **SUBRAMANIAN, Ramesh; 2936 Bayview Run, Oviedo, FL 32765 (US). SETH, Brij, B.; 1641 Indian Dance Court, Maitland, FL 32751 (US).**
- (74) Agents: **MUSONE, John P. et al.; Siemens Corporation, Intellectual Property Dept., 186 Wood Ave. South, Iselin, NJ 08830 (US).**
- (81) Designated States (*national*): **CA, JP.**
- (84) Designated States (*regional*): **European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).**
- Published:**
- *without international search report and to be republished upon receipt of that report*
 - *entirely in electronic form (except for this front page) and available upon request from the International Bureau*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: **THERMAL BARRIER COATING RESISTANT TO SINTERING**



(57) Abstract: A device (10) is made, having a ceramic thermal barrier coating layer (16) characterized by a microstructure having gaps (18) with a sintering inhibiting material (22) disposed on the columns (20) within the gaps (18). The sintering resistant material (22) is stable over the range of operating temperatures of the device (10), is not soluble with the underlying ceramic layer (16) and is applied by a process that is not an electron beam physical vapor deposition process.

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THERMAL BARRIER COATING
RESISTANT TO SINTERING

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part application of U.S. Serial No. 09/245,262 filed on February 5, 1999.

FIELD OF THE INVENTION

This invention relates generally to the field of thermal barrier coatings (TBC), and more particularly to a thermal barrier coating for very high temperature applications, such as combustion turbine engines. In particular, this invention relates to the field of multi-layer ceramic thermal barrier coatings resistant to sintering damage used for coating superalloy components of a combustion turbine. These TBCs are applied by inexpensive processes selected from the group consisting of: ceramic processing techniques, such as sol-gel techniques; vapor deposition techniques, such as chemical vapor deposition; and, preferably, thermal spraying techniques, such as air plasma spraying (APS), where induced vertical gaps in the TBC surface microstructure are prevented from sintering in service, to ensure strain tolerance during use.

BACKGROUND OF THE INVENTION

The demand for continued improvement in the efficiency of combustion turbine and combined cycle power plants has driven the designers of these systems to specify increasingly higher turbine inlet temperatures. Although nickel and cobalt based superalloy materials are now used for components in the hot gas flow path, such as combustor transition pieces and turbine rotating and stationary blades, even these superalloy materials are not capable of

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surviving long term operation at temperatures sometimes exceeding 1000°C.

It is known in the art to coat a superalloy metal component with an insulating ceramic material to improve its ability to survive high operating temperatures; see, for example, U.S. Patent 4,321,310 (Ulion et al). It is also known in the art to coat the insulating ceramic material with an erosion resistant material to reduce its susceptibility to wear caused by the impact of the particles carried within the hot gas flow path; see, for example, U.S. Patents 5,683,825 (Bruce et al.) and 5,562,998 (Strangman). U.S. Patent Application Serial No. 09/393,417, filed on September 10, 1999 (Docket No. T2-98-25, ESCM-283139-00223, Ramesh Subramanian), taught air plasma sprayed TBC coatings of 50 micrometer to 350 micrometer thickness, applied to superalloy base substrates, for turbine application. There, the TBC coating had a planar grained microstructure, where an overlay was allowed to infiltrate the TBC bulk, completely or partially fill microcrack volumes generally parallel to the superalloy base substrate, and finally react with the TBC material. This was to provide a sintering inhibitor, as well as a coating with a low thermal conductivity, which is also erosion and corrosion resistant.

Much of the development in this field of technology has been driven by the aircraft engine industry, where turbine engines are required to operate at high temperatures and are subjected to frequent temperature transients as the power level of the engine is varied. A combustion turbine engine installed in a land-based power generating plant is also subjected to high operating temperatures and temperature transients, but it may also be required to operate at full power and at its highest temperatures for very long periods of time, such as for

days or even weeks at a time. Prior art insulating systems are susceptible to degradation under such conditions at the elevated temperatures demanded in the most modern combustion turbine systems.

In particular, with regard to air plasma sprayed (APS) TBC's, due to repeated thermal cycling, these coatings have to readily accommodate the thermal expansion mismatch stresses and thermal strains to remain adherent to the superalloy substrate. Typical APS coatings achieve this by porosity which is deliberately introduced during the deposition process, such as inter splat boundaries and micro-cracks within the ceramic splats. With increasing demands for higher efficiency of engines, the gas path temperatures are expected to rise and consequently the temperatures at the surface of the ceramic TBC. Higher temperatures would then lead to accelerated sintering of cracks and pores in the APS coatings, especially at the surface. Sintering results in densification of the coating and can lead to its early spallation, due to its reduced capacity to accommodate thermal cycling. Stresses due to thermal cycling can be relieved by vertical cracks through the coating, which increases the thermal cyclic life of the coating.

These vertical cracks in APS coatings can result during the air plasma spraying process, as described in the many articles published in the field of thermal barrier coatings, for example, "Thermal Spray: Advances in Coatings Technology - Experimental and Theoretical Aspects of Thick Thermal Barrier Coatings for Turbine Applications," G.J. Wilms et al., Proceedings of the National Thermal Spray Conference, September 14-17, 1987, Ed. D.L. Houck pp. 155-166. There, APS spraying at high substrate temperatures was described as inducing vertical segmentation cracks which form while relieving shrinkage stresses within the

deposited TBC upon cooling. Initiation of segmentation cracks during APS spraying at high substrate temperatures of the TBC is shown in Figs. 12 and 13 of the Wilms et al. article, where a brick-like microstructure is shown, and also in Figs. 3 and 4 where a more monolithic structure is shown, as in Fig. 6. Preferred thick TBC's, over about 2 mm, are described as being dense, less than 15% porosity, but where individual planar platelets are microwelded to each other and connected to their sublayers with a fine network of vertical segmentation cracks, rather than being porous, about 20% or greater porosity.

Coatings deposited by the APS process, with vertical cracks are called segmented TBCs. Formation of vertical cracks in APS coatings are also discussed in U.S. Patents 4,457,948; 5,073,433; 5,743,013 and 5,839,586 (Ruckle et al., Taylor, Taylor et al. and Gray et al., respectively), in European Patent 0 705 912 A2, and also in "Crystalline Growth Within Alumina and Zirconia Coatings with Coating Temperature Control During Spraying," A. Haddadi et al., Thermal Spray: Practical Solutions for Engineering Problems, C.C. Brendt (Ed.), ASM International, Materials Park OH, 1996, pp. 615-622; "Taguchi Analysis of Thick Thermal Barrier Coatings," J.E. Nerz et al., Thermal Spray Research and Applications, Proc. 3rd National Thermal Spray Conference, Long Beach CA, 1990, pp. 669-673; and "Enhanced Atmospheric Plasma Spraying of Thick TBCs by Improved Process Control and Deposition Efficiency," E. Lugscheider et al., Proc. 15th International Thermal Spray Conference, 1998, pp. 1583-1588.

J. Wigren et al., in "A Combustor Can with 1.8 mm Thick Plasma Sprayed Thermal Barrier Coatings," International Gas Turbine and Aeroengine Congress and Exhibition Proceeding, American Society of Mechanical Engineers, 1998, pp. 1-10, taught a series of temperature

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cycles between 330°C and 340°C over time to induce branched segmentation cracks, for thick protective TBC coatings on combustor walls. Such branchings were also described by J. Wigren et al. in "Thermal Barrier Coatings - Why, How, Where and Where To," Proceedings of the 15th International Thermal Spray Conference, pp. 1531-1542, May 25-29, 1998, where it was pointed out that sophisticated TBC's have raised the temperature capability of gas turbines by about 500°C in the last 15 years.

While these patents and articles discuss induced microcracks in ceramic coatings, other articles discuss filling such microcracks, primarily to act as seals to corrosive agents, for example, "Effects of Sealing Treatment and Microstructural Grading upon Corrosion Characteristics of Plasma Sprayed Ceramic Coating," Y. Kimura et al., Proc. 7th National Thermal Spray Conference 1994, pp. 527-536; "Sealing of Plasma Sprayed Ceramic Coatings by Sol-Gel Process," K. Moriya et al., 7th National Thermal Spray Conference 1994, 549-553; and "Ceramic Impregnation of Plasma Sprayed Thermal Barrier Coatings," J. Karthikeyan et al., Thermal Spray: Practical Solutions for Engineering Problems, ASM International, 1996, pp. 477-482.

The above-mentioned patents articles, however, do not address the possibility of sintering the vertical cracks and the subsequent loss in strain compliance with increasing operating temperatures.

Accordingly, it is an object of this invention to make a device which is capable of operating at temperatures in excess of 1200°C for extended periods of time, with reduced component degradation. It is also an object of this invention to provide a method of producing such a device that utilizes only commercially available material processing steps and inexpensive deposition techniques,

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such as APS, rather than electron beam physical vapor deposition ("EB-PVD"). The APS process basically involves spraying TBC powders, such as stabilized zirconia, after passing them through a plasma gun.

SUMMARY

These and other objects of the invention are achieved by providing a method for producing a device operable over a range of temperatures which comprises the steps: providing a substrate; optionally, coating a bond coat layer on the substrate; coating a ceramic layer at least 50 micrometers thick on the bond coat layer or the substrate by a process selected from the group consisting of ceramic processing techniques, vapor deposition techniques and thermal spray techniques, in a manner that provides said ceramic layer with a microstructure characterized by a plurality of vertical and horizontal gaps, where the vertical gaps provide a columnar structure extending from the outer surface to at least about 1/3 of the thickness toward the substrate; and depositing, at least, within the vertical gaps a sintering inhibiting material, where the majority of vertical and horizontal gaps are not closed. If a bond coat is not used, the ceramic layer can be applied directly to the substrate.

This invention has the potential to extend the operating temperature capabilities and durability of turbine engines beyond the current state of the art, air plasma spray (APS) 8 wt. % yttrium stabilized zirconia TBC. It involves the deposition of ceramic coatings with horizontal and—predominantly—vertical gaps and the infiltration of these predominantly vertical cracks with a sintering inhibitor. Upon operation at high temperatures, where sintering or closing up of the cracks could occur leading to a loss in strain tolerance, the sintering inhibitor is expected to prevent closure of the vertical

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ceramic material is infiltrated onto the vertical and horizontal micro crack gaps resulting from air plasma spraying; and

Figure 3 is a greatly enlarged view of the surface of the thermal barrier coating.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

When prior art thermal barrier coating systems are exposed to the high temperature environment of the hot gas flow path of a land-based combustion turbine power plant, one of the reasons for failure of the thermal barrier coating is sintering of the ceramic TBC and consequent loss in strain tolerance. A current state-of-the-art thermal barrier coating is yttria stabilized zirconia (YSZ). The YSZ may be applied in this invention by thermal spray processes such as new and improved air plasma spray APS, inductively coupled plasma processes, high power and high velocity plasma processes, or by vapor deposition processes such as chemical vapor deposition CVD, MOCVD, or by ceramic processing techniques such as sol-gel, all now well known in the art. These techniques can provide a predominantly vertical (in relation to the substrate) columnar microstructure at the outside surface of TBCs and also create a series of submicron sized horizontal cracks within the YSZ layer intersecting the columnar microstructure. For the purposes of this application, the terms "gap" is meant to include not only the gaps between adjacent columns in a columnar microstructure, but also horizontal cracks resulting from APS or similar processes. The amount of vertical and horizontal gaps in the TBC can be accurately controlled by modification of deposition parameters.

The gaps provide a mechanical flexibility to the ceramic TBC layer. During operation at high temperatures, it is known that these gaps have a tendency to close, and

if the device is maintained at the elevated temperature for a sufficient length of time, the adjacent sides of the gaps will bond together by sintering. The bonding of the ceramic material across the gaps reduces the strain compliance of the ceramic coating, thereby contributing to failure of the coating during subsequent thermal transients.

Referring now to FIG. 1, one component device of a turbine is shown. Turbine blade 10 has a leading edge 13 and an airfoil section 17, against which hot combustion gases are directed during operation of the turbine, and which is subject to severe thermal stresses, oxidation and corrosion. The root end 19 of the blade anchors the blade. Cooling passages 21 may be present through the blade to allow cooling air to transfer heat from the blade. The blade itself 10 can be made from a high temperature resistant nickel or cobalt based superalloy 12, shown in Fig. 2, such as, a combination of Ni-Cr-Al-Co-Ta-Mo-W.

A bond coat 14 could cover the body of the turbine blade 12, which could then be covered by the thermal barrier coating 16, all shown in Fig. 2. The barrier layer of this invention, as well as the bond coat (or base coat) and other protective coating can be used on a wide variety of other components of turbines, such as, turbine vanes, turbine transitions, or the like, which may be large and of complex geometry, or upon any substrate made of, for example metal or ceramic, where thermal protection is required.

Figure 2 illustrates a cross-sectional view of a portion of a device having a thermal barrier coating, TBC 16, which is less susceptible to a reduction of strain compliance due to sintering. Preferably the TBC 16 will be at least 50 micrometers thick, to allow superior insulating and protective properties for the underlying substrate.

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The device 10 has a substrate 12 that may be made of a superalloy metal or other material having the desired mechanical and chemical properties.

Disposed on the substrate 12 is an optional bond coat layer 14. In some applications the bond coat layer 14 may be integral with the substrate 12. In combustion turbine applications the bond coat layer 14 may typically be an MCrAlY layer deposited by an EB-PVD, sputtering or low pressure plasma spray process. As is known in the art, the M in this formulation may represent iron, nickel or cobalt, or a mixture thereof. Alternatively, the bond coat layer 14 may be platinum or platinum aluminide, or there may be no distinct bond coat layer. Disposed on the bond coat layer, or directly on the substrate 12 in the absence of a bond coat layer 14, is a ceramic layer 16 which serves to thermally insulate the substrate 12 from the hostile environment in which it operates. The ceramic layer 16 is preferably formed of a YSZ material, for example 8 weight % yttria stabilized zirconia as is known in the art, or other TBC material, deposited by a new and improved APS process, to form a columnar microstructure characterized by a plurality of gaps 18 between adjacent columns 20 of YSZ or other material. An oxide scale 15 is also shown, being formed from the bond layer 14, and which further protects the substrate from oxidative attack. As shown, the columns 20 provide a columnar structure extending from the outer surface 23 distance 25 which is at least about 1/3 of the thickness toward the substrate 12.

As shown in Figure 3, the TBC layer of the device also includes a sintering inhibiting material coating 22 disposed within the predominantly vertical gaps 18, but not generally bridging across the gaps from one column to the adjacent column. This sintering inhibiting material 22 will also coat the generally horizontal gaps 30. By

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sintering resistant material in this application it is meant any material which is more resistive to sintering than the TBC material 12. The sintering inhibiting material 22 may be a ceramic material that is stable over the range of temperature in which the device 10 is operated, for example ambient air temperature to over 1200°C, and as high as 1500°C. By stable in this application it is meant that the material does not undergo a crystallographic phase transformation when exposed to the full range of its design operating temperatures.

United States Patent 5,562,998 (Strangman) discussed previously teaches the application of a bond inhibitor coating over a ceramic thermal barrier coating. The bond inhibitor described in that patent is an unstabilized material, such as unstabilized zirconia or unstabilized hafnia. These materials will sinter or bond together during high temperature operation, but upon cooling to lower or ambient temperatures, these materials will cycle through a disruptive tetragonal monoclinic phase transformation. This transformation tends to break the bonds between adjacent columns. While such materials may be effective for aircraft engines that have short thermal cycles, they may be unsuitable for land based power generating engines which have longer operating cycles. During long term exposure to high temperatures, unstabilized zirconia and hafnia will dissolve into the underlying YSZ material.

Once dissolved into the ceramic insulating material, the bond inhibitor material of the 5,562,998 patent is no longer available to undergo a crystallographic transformation within the gaps upon cooling. Thus, after extended periods of high temperature operation, the sintered bonds are not broken, consequently reducing the

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strain compliance of the ceramic insulating material and leading to premature failure of the component.

Furthermore, prior art United States Patent 5,683,825 (Bruce et al.), discussed above, discloses an erosion resistant thermal barrier coating. In that patent, an erosion resistant composition such as alumina or silicon carbide is disposed on top of a ceramic insulating layer. That patent describes a relatively thick coating of erosion resistant material that does not penetrate between the columns of the underlying ceramic insulating material, and therefore does not act to prevent sintering between the columns.

The sintering inhibiting material 22 of the present invention overcomes these deficiencies in the prior art. By infiltrating a sintering inhibiting material 22 into the gaps 18 and 30 and preventing the bonding of adjacent columns 20, there is no need to rely upon a crystallographic transformation to break the bonds as in the prior art. Sintering inhibiting material 22 is preferably an oxide compound which is insoluble with the underlying ceramic layer 16, and which is stable over the range of temperatures of operation of device 10. One such sintering inhibiting material 22 for use with a ceramic layer 16 of YSZ is aluminum oxide (alumina) Al_2O_3 . An alternative embodiment for the sintering inhibiting material 22 is yttrium aluminum oxide.

The sintering inhibiting material 22 may be infiltrated into the gaps 18 via a metal organic chemical vapor deposition (CVD) process. The CVD process is used to deposit the sintering resistant material 22 to a thickness on the top surface 23 of the columns 20 of ceramic layer 16 of YSZ is aluminum oxide (alumina) Al_2O_3 . The sintering inhibiting material 22 may be infiltrated into the gaps 18 via a metal organic chemical vapor deposition (CVD)

process. The CVD process is used to deposit the sintering resistant material 22 to a thickness on the top surface of the columns 20 of ceramic layer 16 ranging from no more than a few angstroms to several micrometers. In one embodiment an alumina layer having a thickness of approximately 5 micrometers on the top surface of the columns 20 of the ceramic layer 16 may be used. Alternative embodiments may have a thickness of sintering resistant material on the top surface of the columns 20 of ceramic layer 16 of no more than 0.1 micrometer, or alternatively no more than one micrometer, or alternatively no more than 10 micrometers. The thickness of the coating of sintering resistant material 22 within the gaps 18 will be less than but generally proportional to the thickness on the surface of the ceramic layer 16. The thickness should be controlled to prevent the sintering resistant material 22 from bridging across the gaps 18, such as shown at points 34 thereby degrading the performance of the coating. Because the selected sintering inhibiting material 22 does not readily sinter, the columns 20 of device 10 will not bond at high temperatures. And because the sintering inhibiting material 22 is not soluble with the underlying material of ceramic layer 16, it is maintained at the surface of the columns 20 throughout the life of the device 10, thus maintaining its resistance to sintering.

The sintering inhibiting material 22 may be applied to the insulating ceramic layer 16 as an intermediate amorphous or unstable phase. In one embodiment of the invention, amorphous alumina is deposited within the gaps 18 by a metal organic CVD process. Upon heating, either during the manufacturing process or during the initial operation of the device 10, the amorphous coating undergoes a transformation to a crystallographically stable phase, such as alpha Al_2O_3 . It

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is alpha phase that is stable at high temperatures and that performs the function of a sintering inhibitor.

The method for producing a device according to this invention utilizes processes that are commercially available. To produce such a device, a substrate 12 may, optionally, first be coated with a bond coat 14, or directly onto the substrate if no bond coat is used, by a known process such as a low pressure plasma spray, high velocity oxygen fuel, shrouded plasma spray or air plasma spray process. The ceramic TBC layer 16 is then disposed on the bond coat 14 by known improved APS processes which simultaneously utilizes a plasma to melt the ceramic particles of a carrier gas and to deposit the particles onto the substrate. Several modifications to the spray parameters—such as voltage, current, particle velocity and substrate temperature—can control the function of horizontal and vertical cracks.

This improved APS process provides a ceramic TBC layer 16 having a plurality of gaps 18 and 30 therewithin. The sintering inhibiting material 22 is then applied to the surface of the columns 20 by a vapor deposition technique such as chemical vapor deposition or metal organic CVD, or by one of a number of known infiltration techniques such as sol-gel infiltration.

Preferably, the sintering inhibiting material 22 may be applied as a continuous coating within the gaps 18, either as an amorphous or a stable phase. Figure 2 illustrates an alternative embodiment of a device in accordance with this invention. Like structures are numbered consistently between the two Figures. As seen in Figure 2, a substrate 12 having an optional bond coat 14 disposed thereon is coated with a ceramic layer 16.

While not shown in the drawings, the inhibiting material can also be disposed within the gaps 18 as a

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plurality of nodules which may demonstrate a reduced tendency to form bridges between column 20 due to a lesser contact area between nodules on adjacent columns when compared to a continuous coating of sintering inhibiting material. However, any formation of intermittent bridges between columns 18 can break easily upon regular thermal cycling of device 10. The nodular morphology is achieved by controlling the thickness of the applied coating of material and the subsequent heat treatment. For example, a relatively thin coating of approximately 0.1 micrometer of alumina at the top surface 23 of the ceramic layer 16 will result in a relatively thin continuous layer in the gaps 18.

During the subsequent heat treatment, as the alumina converts to the stable alpha phase it undergoes a volume reduction which tends to create nodules of sintering resistant material within the gaps. A thicker coating of approximately 1 micrometer of alumina at the surface will provide a thick enough coating within the gaps 18 that even after heat treatment the sintering resistant material 22 to remain as a continuous coating. An alternative method of achieving a continuous coating within the gaps 18 is to apply multiple thin layers of the sintering resistant material so that any space is essentially filled with to create a continuous coating 22.

In the embodiment of Figure 3, the sintering inhibiting material is disposed within only a top portion of gaps 18 and not a bottom portion of gaps 18. The geometry of the gaps 18 and the process for depositing the coating will control this variable. Preferably in this process the improved APS process will cause the sintering inhibiting material to coat the interior gaps 18 and 30 to a substantial extent, at least 1/10 the thickness of the thermal barrier layer 16.

Other aspects, objects and advantages of this invention may be obtained by studying the Figures, the disclosure, and the appended claims.

WHAT IS CLAIMED IS:

1. A method for producing a device operable over a range of temperatures, the method comprising the steps of:

providing a substrate (12);

optionally, coating a bond coat layer (14) on the substrate (12);

coating a ceramic layer (16) at least 50 micrometers thick on the bond coat layer or the substrate by a process selected from the group consisting of ceramic processing techniques, vapor deposition techniques, and thermal spray techniques, in a manner that provides said ceramic layer with a microstructure characterized by a plurality of vertical and horizontal gaps (18,30), where the vertical gaps provide a columnar structure extending from the outer surface to at least about 1/3 of the thickness toward the substrate (12); and

depositing within said vertical and horizontal gaps (18,30) a sintering inhibiting material (22), where the majority of vertical and horizontal gaps (18,30) are not closed.

2. The method of claim 1, wherein the step of depositing a sintering inhibiting material (22) further comprises depositing a sintering inhibiting material that is stable over said range of temperatures, and wherein a bond coat layer (14) is applied to the substrate (12).

3. The method of claim 1, wherein the step of depositing a sintering inhibiting material further comprises the step of depositing a sintering inhibiting material that is insoluble with said ceramic layer.

4. The method of claim 1, wherein the step of depositing a sintering inhibiting material (22) further comprises depositing said sintering inhibiting material as a continuous coating within said gaps (18,30).

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5. The method of claim 1, wherein the step of depositing a sintering inhibiting material (22) further comprises depositing aluminum oxide.

6. The method of claim 1, wherein the step of depositing a sintering inhibiting material (22) further comprises depositing yttrium aluminum oxide.

7. The method of claim 1, wherein said ceramic layer (16) comprises a segmented microstructure, and wherein the step of depositing a sintering inhibiting material (22) further comprises depositing said sintering inhibiting material on the surface (23) of the columns (20) of said ceramic layer to prevent the sintering of gaps during the operation of said device.

8. The method of claim 1, wherein the step of depositing a sintering inhibiting material (22) further comprises the steps of:

depositing a sintering inhibiting material (22) in an unstable phase; and

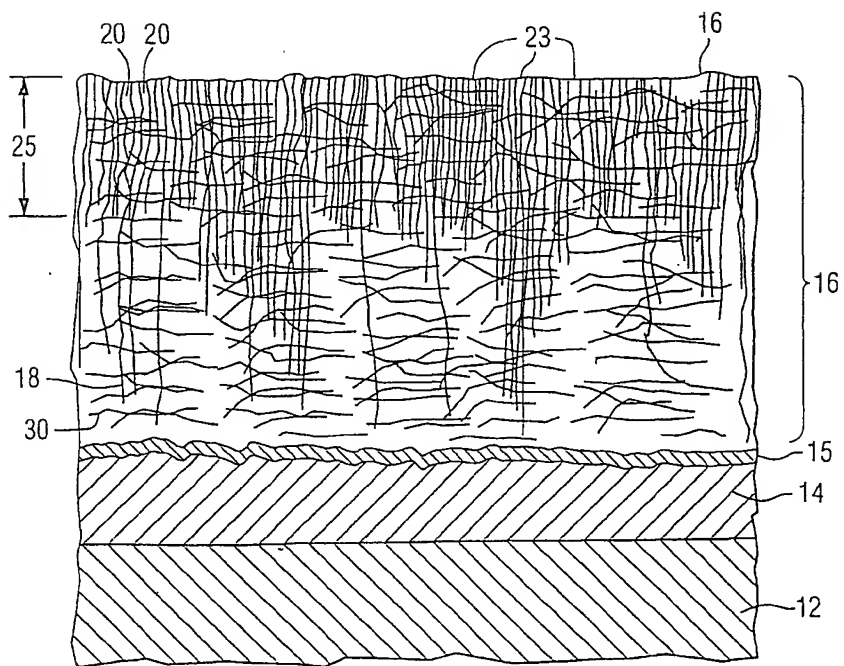
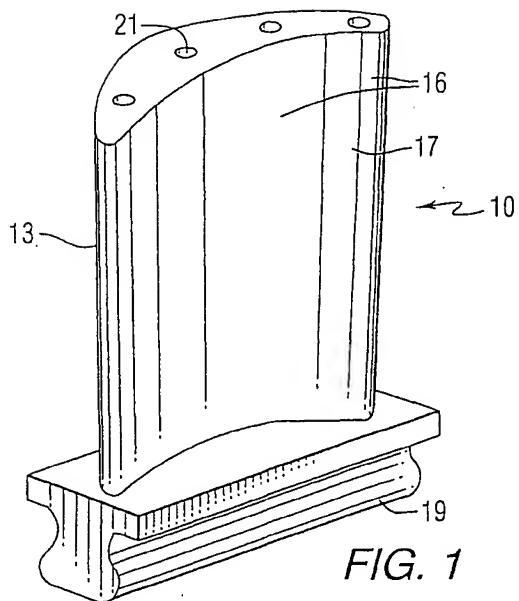
heat treating said sintering inhibiting material to obtain a sintering inhibiting material which is stable over said temperature range.

9. The method of claim 1, wherein the step of coating the ceramic layer (16) is by a process selected from the group consisting of air plasma spraying, chemical vapor deposition and sol-gel techniques.

10. The method of claim 8, wherein the step of heat treating is performed during the operation of said device.

11. The method of claim 9, wherein the step of coating the ceramic layer (16) is by air plasma spraying.

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